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INTERACTION - PART III
SURFACE CONTAMINATION

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RESEARCH ON MOLECULE-SURFACE INTERACTION

PART III

SURFACE CONTAMINATION

by

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September 1964

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Approved by: *Charles E. Mack, Jr.*
Charles E. Mack, Jr.
Director of Research

FOREWORD

This Memorandum comprises the third part of a three-part final report on NASA contract number NASw-709. It describes one part of the experimental work performed under that contract, which is a successor to NASr-104 on the same subject, namely, the interaction of high energy gas particles with solid surfaces.

This research was performed under the technical supervision of the NASA Physics of Fluids Office, Mr. Alfred P. Gessow, Chief. It covers the period from July 1, 1963 to August 9, 1964.

ABSTRACT

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Experiments leading to the design of an apparatus for the preparation and photoelectric analysis of atomically clean metallic specimens are described. The system arrived at contains two electron guns, provisions for measuring very small currents (10^{-16} amps) and means for introducing monochromatic ultraviolet light, electrical potentials, and ultra pure gases. Probable effects of surface contaminants on molecule-surface interactions and plans for incorporating surface preparation techniques into a shock tube driven molecular beam apparatus are also discussed.

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INTRODUCTION

Defining surface conditions on an atomic scale is an important requirement of most research on interfacial phenomena. The interaction of atoms and molecules with surfaces plays a much more important role in the upper atmosphere than it does at lower altitudes. At heights of about 100 to 400 kilometers the mean free paths range from 10 to 10^5 cm so gas-surface collisions become much more important than gas-gas collisions, even on large configurations. At these altitudes the main atmospheric constituents, oxygen and nitrogen, exist in both molecular and atomic forms. The interaction of molecular and atomic particles with hypervelocity vehicle surfaces is dominated by the uppermost layers of the surface.

Atoms adsorbed on the surface can significantly modify the surface properties and strongly influence the resulting interaction through several mechanisms. The binding energy between the adsorbed layer and the solid is often considerably different than that for the surface atoms of the solid. This in turn changes the dynamic response of the lattice to the impulsive interaction (Refs. 1 and 2). In addition, the effective atomic diameter of the interacting species plays a significant role in determining momentum accommodation (Ref. 3). The work of Sinanoglu and Pitzer (Ref. 4) indicates that when an atom is adsorbed on a surface the interaction (Lennard-Jones) potential is modified by the perturbing effect of the surface fields. In addition chemical phenomena (such as recombination and dissociation) and the surface topography certainly require consideration in the formulation of the boundary conditions for hypervelocity free-molecule flow. Early experiments attempting to measure thermal accommodation coefficients of various surfaces with respect to different atomic and molecular gas species appear to differ widely from laboratory to laboratory. More recent and better controlled experiments indicate that the condition of the surface is a dominant variable capable of influencing the results by as much as an order of magnitude.

With this knowledge in mind, we have undertaken to design and fabricate an experimental system. The immediate function of the system will be to prepare and characterize atomically clean surfaces (Refs. 5 and 6). This will be attempted in an ultrahigh vacuum environment ($< 10^{-9}$ mm Hg) by a combination of electron and/or ion bombardment, high temperature heating, and annealing. The cleaning

process will be monitored by measuring the changes in surface photoelectric effect which is very sensitive to changes in the surface electric dipole moment. The treatment procedures thus developed will then be adapted for use in our shock-tube-driven molecular beam apparatus, so that surface condition will be controlled in those experiments. This molecular beam is of the impulsive flow type, with a test duration of at most a few milliseconds. It therefore appears feasible to clean a surface immediately before a run, and a negligible contamination either from the environment ($\sim 10^{-7}$ mm Hg) or the test itself ($< 10^{14}$ impacts/cm²) can be ensured. In addition, a controlled contamination can be achieved by waiting a prescribed interval in a controlled environment.

The sensitivity of the photoelectric work function to surface contamination is related to the exact configuration of the electrical charges near the surface. The work function of a metal is usually taken to be the minimum amount of energy necessary to remove an electron which is near the surface of the metal. A double layer of charge exists at the surface of an ideal metal. The fields associated with this layer contribute to the magnitude of the work function. Differences in the work function among different crystal faces of the same metal are due to differences in the double layer existing on those faces. Adsorbed atomic and molecular species modify the surface double layer; even van der Waals adsorption may produce changes. Experimental data suggest that the magnitude of work function is determined more by the adsorbed layer than by the nature of the substrate.

EXPERIMENTS

To facilitate the design of the final apparatus we completed the following three experiments.

Surface Sputtering

We tested in a general purpose vacuum system several possible configurations for producing a useful argon plasma to be employed in the ion bombardment cleaning of a specimen surface. In the final configuration argon ions are drawn to the cylindrical specimen by a suitably applied electric field and sputter impurity atoms from the surface. Figure 1 shows the experimental set up used in this phase of the work.

This vacuum system has allowed us to operate at pressures in the 10^{-6} mm Hg range, but it is incapable of maintaining this vacuum when large gas loads are present for a long and continuous period of time. With the filament ① (see Fig. 4) grounded and at a temperature of about 1750°C , and the collector ② at 150 volts positive with respect to the filament, we measured a collector current of about 2 ma. With the sample ③ at 400 volts negative with respect to element ④, which was also at ground potential, we found no appreciable current in the circuit containing elements ③ and ④. Argon was let into the system through a variable leak and was continually pumped out. With argon gas flowing through the system at between 1×10^{-4} and 1×10^{-3} mm Hg a positive ion current was measured to the polycrystalline copper specimen. This current could be most easily controlled by adjusting the filament temperature, the potential of the specimen, or the argon pressure. It could be increased to about 200 microamps at an argon pressure of about 3×10^{-4} mm Hg and appeared to be very sensitive to the argon pressure. At higher currents, the discharge appeared as a faint blue-purple glow with the intensity of the glow and the current to the sample both reaching a maximum at an argon pressure of 3×10^{-4} mm Hg. As the argon pressure was changed above and below this value the discharge became weaker and finally died out. This effect was reversible, reproducible, and is not completely understood at the present time.

When running at relatively high plasma densities, there was a tendency for arcing to occur between elements during the argon ion bombardment. This was traced to sharp corners which were subsequently

eliminated. The presence of high voltage feedthroughs in the vicinity of the Bayard-Alpert gauge also affected operation. We found that the feedthrough connected to the sample to apply a positive 500 volt potential during ion bombardment drew a current which appeared to originate from the Bayard-Alpert. This was remedied by rearranging the various system components.

In order to obtain a qualitative check on the ion bombardment cleaning, we ran the experiment at about 250 microamperes (argon current) and at 600 volts for about 15 minutes. The polycrystalline copper specimen before treatment had a dull red color. After the experiment it was a bright, lustrous red orange. A thin translucent red film appeared on the wall of the vacuum chamber at F of Fig. 1. The position of the film with respect to the specimen indicated that it was composed of sputtered atoms which came primarily from the front surface of the specimen. Assuming singly charged species, we calculated that the flux of argon ions (I_A) arriving at the specimen was $1.56 \times 10^{15} \text{ cm}^{-2} \text{ sec}^{-1}$.

During the fifteen-minute interval, the total number of argon atoms arriving was therefore about 1.4×10^{18} . Assuming a yield for copper of 1.6 we calculated that the number of copper atoms emitted was 2.24×10^{18} . The geometrical surface area of the film was about 110 cm^2 and one monolayer would require about 5.50×10^{16} Cu atoms. Therefore about 41 monolayers were deposited, which is equivalent to about $1.4 \times 10^{-6} \text{ cm}$ film thickness.

The next step was to attempt to heat the specimen to relatively high temperatures by employing the filament already present in the apparatus. In principle this appears to be a reasonable approach to localized heating of fairly large metallic specimens. However, the radiant heating by the hot filament of other nearby internal parts of the apparatus and contamination of the specimen surface by tungsten boiling off the filament tended to create difficulties. For a filament at a temperature of 2300°K and having a surface area of 1.65 cm^2 the monolayer formation time τ is given by

$$\tau = \frac{N}{N_w} \cdot \frac{\beta}{\epsilon}$$

where N is the number of atoms in a monolayer, N_w the number of tungsten atoms emitted from each square centimeter of the filament per second, ϵ the sticking coefficient and β a geometrical

factor. Taking

$$N = 5 \times 10^{14}, N_w = 7.25 \times 10^{13}, \epsilon = 0.5$$

then

$$\tau = 6.9 \beta \text{ sec.}$$

This estimate represents close to the upper limit of tungsten contamination. The parameter β may be minimized by placing the filament off-axis or by mechanically shielding it from the specimen. We chose the latter.

If a metal foil is placed in front of the filament, the specimen should see none of the tungsten atoms; however, the efficiency of the filament defined as total electron emission from the filament (I_t) per electron received at the anode (I_s) would be drastically decreased. To minimize this we use two deflector electrodes symmetrically placed about the filament so as to draw the electrons around the foil. The collector is made of 0.005" tantalum foil which has good mechanical properties and a relatively low vapor pressure at high temperatures. The foil is an effective heat sink, minimizing heating of internal parts of the system, and it also acts as an electron collector during the ion bombardment procedure. The deflectors and all connectors are 0.030" molybdenum rod. All internal connections have been spot welded. The various dimensions and operating voltages have been optimized in a semi-empirical manner so as to maximize the efficiency of the gun.

High Temperature Heating and Annealing

As part of the cleaning procedure it may be necessary to heat the specimen so as to attempt to anneal out any defects introduced into the surface due to the ion bombardment procedure. In addition, high temperature heating of the specimen should drive occluded argon atoms from the surface.

The controlled heating of the specimen was accomplished by employing the electron gun. This was done by moving the sample so that it was in front of the filament. The specimen was maintained at about +1.5 kilovolts with respect to the filament, which was at ground potential. The filament temperature was raised until the current to the sample was about 15 ma. This represented a power

input to the specimen of about 22.5 watts. The resulting violent outgassing was too much for the small pumps in our temporary system to handle. The increase in background pressure gave rise to a large heat loss from the sample due to conduction, and contributed to preventing the sample temperature from rising above several hundred degrees centigrade. In our final setup the primary heat loss should be radiation. This loss will be about $8\frac{1}{2}$ watts/cm² for unit emissivity at 1100°K. The surface area of the sample is about 11 cm and the emissivity of an oxidized polycrystalline nickel surface is about 0.5, so the total radiant power will be about 50 watts. This indicates that a larger power input is necessary to reach the desired temperature. An identical second gun structure was fabricated and placed diametrically opposite the first. During the ion bombardment procedure, one gun structure is operating while the collector of the other acts as the anode for the first gun. Element ④ in Fig. 1 was removed without materially affecting the system performance. With an improved pumping system and the simultaneous operation of both guns, the sample was easily and rapidly heated to about 1100°K.

Photoelectric Measurements

The purpose of this experiment was to measure the spectral distribution of the photoelectric yield and the work function. The technique involved directing a beam of monochromatic radiation onto the specimen surface and measuring the current generated (Fig. 2).

The photoelectric measurements were performed on an untreated cylindrical polycrystalline nickel specimen mounted within a system in which the pressure was usually held in the 10^{-6} mm Hg region. The light source was a high power compact arc lamp which was mounted in a temporary housing. The light intensity at 5780Å was found to vary parabolically with power input between 150 and 300 watts. All light intensity measurements were made with a thermopile whose sensitivity was virtually independent of wavelength. The output of the bulb could be focused on the slit system of either of two quartz prism monochromators, one of which was a single and the other a double prism instrument. At small slit widths (below 0.5 mm) the single prism monochromator alignment was very critical. Measurements of the light intensity as a function of wavelength were made between 2400Å and 6000Å. In general these

were in reasonable accord with available data; however, above about 4500Å it was difficult to make comparisons due to the poor performance of the quartz prism. The lowest wavelength line which could be detected and resolved with this setup was at 2968Å, and this was with a band pass of about 45Å. At 2400Å and with a 20Å band pass the intensity was one third that at 2968Å and was at the lower limit of the detecting device used. There were no special problems with the monochromator except that to obtain a small band pass the light intensities became immeasurably small.

Upon completion of the spectral distribution measurements, the single prism monochromator output was focused onto the surface of the sample through a quartz window which had been cemented to the vacuum system. The light absorbed by the electrons at the metal surface gave rise to currents of the order of 10^{-15} amp; and changes in current of the order of 10^{-16} amps were measured. This was accomplished by a vibrating reed electrometer by allowing the charge on the condensor to leak through a 10^{12} ohm resistor and measuring the voltage drop across the resistor. The time constant of the circuit was about 2 sec. In order to make the necessary measurements the instrument had to be very carefully shielded, grounded, and isolated from extraneous electrical signals. After taking these precautions, we found that varying stray capacitance effects were still present. Movement in the vicinity of the experiment caused noticeable disturbances. During the measurement of the photoelectric yield as a function of wavelength the electrometer was fairly stable and the measurements indicated a long wavelength threshold of about 2570Å, corresponding to a work function of 4.81 eV. This is consistent with other measurements on untreated nickel specimens. It should be noted that the cutoff is not a very sharp feature of the photoelectric yield curve, the current seeming to tail off and merge into the background. This problem has been treated theoretically in a relatively simple semiclassical fashion in 1932 by Fowler (Ref. 7). Recently it has been subjected to some criticism (Ref. 8) and is currently being thoroughly reinvestigated.

The same experiments were repeated with a double prism monochromator. Due to the greater dispersion of this instrument alignment problems were considerably reduced. A plot of light intensity at 3660Å versus slit width was linear down to a slit width of 0.15 mm which is as low as measurements could be made. The instrument was clearly able to resolve the line at 2895Å while lines as low as 2483Å could be observed even though they were at the lower limit of the detecting system. The photoelectric threshold measurements showed a sharper cutoff indicating less stray

light present in the monochromator output. The long wavelength threshold was at about 2550A corresponding to a work function of 4.84 EV. The results obtained with the two monochromators indicated that for our purposes it would be preferable to employ the doubly dispersing instrument. The alignment requirements are not as severe, resolution is increased by a factor of two and scattered light is reduced to a reasonable level. The only advantages the single prism instrument offered were that it was not necessary to employ a water filter between the light source and the entrance slit, and a somewhat lower cost.

DESIGN OF THE SURFACE PREPARATION APPARATUS

The surface preparation apparatus consists of three major sections:

Primary vacuum producing and measuring components

Gas handling system

Test chamber.

Primary Vacuum Producing and Measuring Components

The primary vacuum producing and measuring components are illustrated in Fig. 3. The three-stage self-fractionating oil diffusion pump is isolated from the mechanical pump by a liquid nitrogen cold trap. The working fluid is a low vapor pressure butyl thylate oil (trade name Convalex-10) possessing good cracking characteristics. The expansion chamber permits one to turn off the mechanical pump when the system is at ultrahigh vacuum without undue backpressure buildup on the low vacuum side of the diffusion pump. Dual copper foil cold traps minimize backstreaming of oil vapors into the test chamber and gas handling system. The magnetically operated glass ball valve I and the 1-inch all metal bakeable valve J isolate the primary pumping system from the test chamber and gas handling system. This pumping system is expected to evacuate the system to at least the 10^{-8} mm Hg range. The pressure may be monitored by either a glass thermocouple gauge D or a Nottingham modified Bayard-Alpert gauge K.

Gas Handling System

To minimize pumping times the gas handling system is constructed primarily of 1-inch tubing. It can be isolated from the test chamber by a bakeable variable conductance metal leak. The function of the gas handling system is to introduce known amounts of highly purified gases into the test chamber. The gas is contained in a sealed bottle which may be broken by an externally operated metal hammer. The gas can then be fed into the gas handling network in a controlled manner through a second bakeable all metal leak. The spectroscopically pure gas may be further purified by a zeolite trap and an

active getter film. The getter film is formed (under high vacuum conditions) by flashing a heavy tungsten spiral on which is wound a titanium filament. A one liter pyrex flask 0 in the gas handling system acts as a reservoir for the gas being bled into the test chamber. The pressure in the gas handling system is again measured by a modified Bayard-Alpert gauge. The gas handling system can be baked by surrounding it with an oven to temperatures as high as about 400°C in order to minimize pump-down time.

Test Chamber

The test chamber is demountable from the rest of the system by means of a large 6-inch stainless steel flange. The test chamber contains 1) an optically flat quartz window which allows ultraviolet light to be focused into the chamber, 2) a bakeable sapphire insulated vacuum feedthrough to which is connected a hollow cylindrical nickel electrode capable of collecting currents as low as 1×10^{-16} amperes, 3) two shielded spiral tungsten electron emitters, 4) a cold finger for cryogenically pumping impurity gases, 5) a titanium getter pump which can obtain and maintain ultrahigh vacuum environment in the sealed off test chamber, and 6) two sets of electrical feedthroughs to allow for the introduction of the proper voltages and measurement of the temperature of the various elements contained within the test chamber. The pressure in the test chamber may be monitored by a modified Bayard-Alpert gauge.

The cylindrical metallic specimen to be studied will be supported within the test chamber and have its axis colinear with the chamber axis. The specimen may be translated along the chamber axis by an externally operated magnet. The surface cleaning may be accomplished by an externally supported ion beam and/or by high temperature heating. The cleaning process may be monitored by measurement of the photoelectric yield as a function of wavelength and the change in work function. The hollow nickel sleeve acts as the collector of photoelectrically emitted electrons.

The photoelectric effect will be measured by employing a high power, compact, arc lamp as a source of ultraviolet light. This will be focused onto the slit of a double prism monochromator. The isolated spectral portion may then be either focused onto the specimen surface or onto the quartz window of a vacuum thermopile for measurement of relative spectral intensity. The monochromator,

light source, and focusing arrangement are mounted on an optical bench which is prealigned to the optical axis of the monochromator. The whole arrangement is mounted on a heavy metal slab which allows for the alignment of the exit beam with the axis of the specimen so that near normal incidence is maintained.

CONCLUSIONS AND STATUS

The experiments which have been conducted to date have proven the procedures and equipment proposed for use in our surface preparation apparatus to be satisfactory. We are now in the process of setting up this apparatus, which will be used for evaluating different surface preparation techniques. We hope to use the results of these experiments to design practical preparation and control techniques for use in our molecular beam apparatus (Ref. 1).

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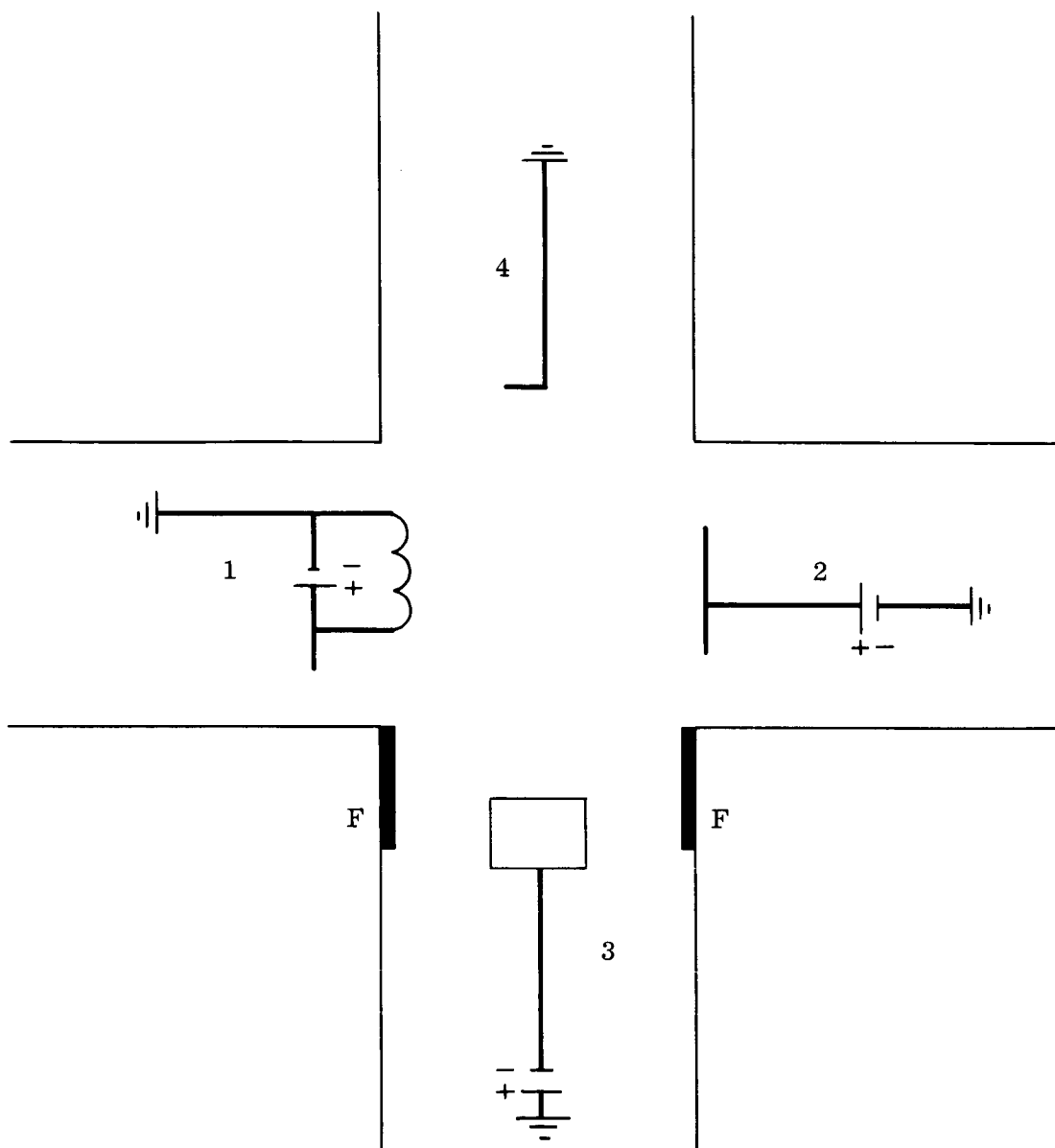


Fig. 1 Schematic of Ion Bombardment Experiment

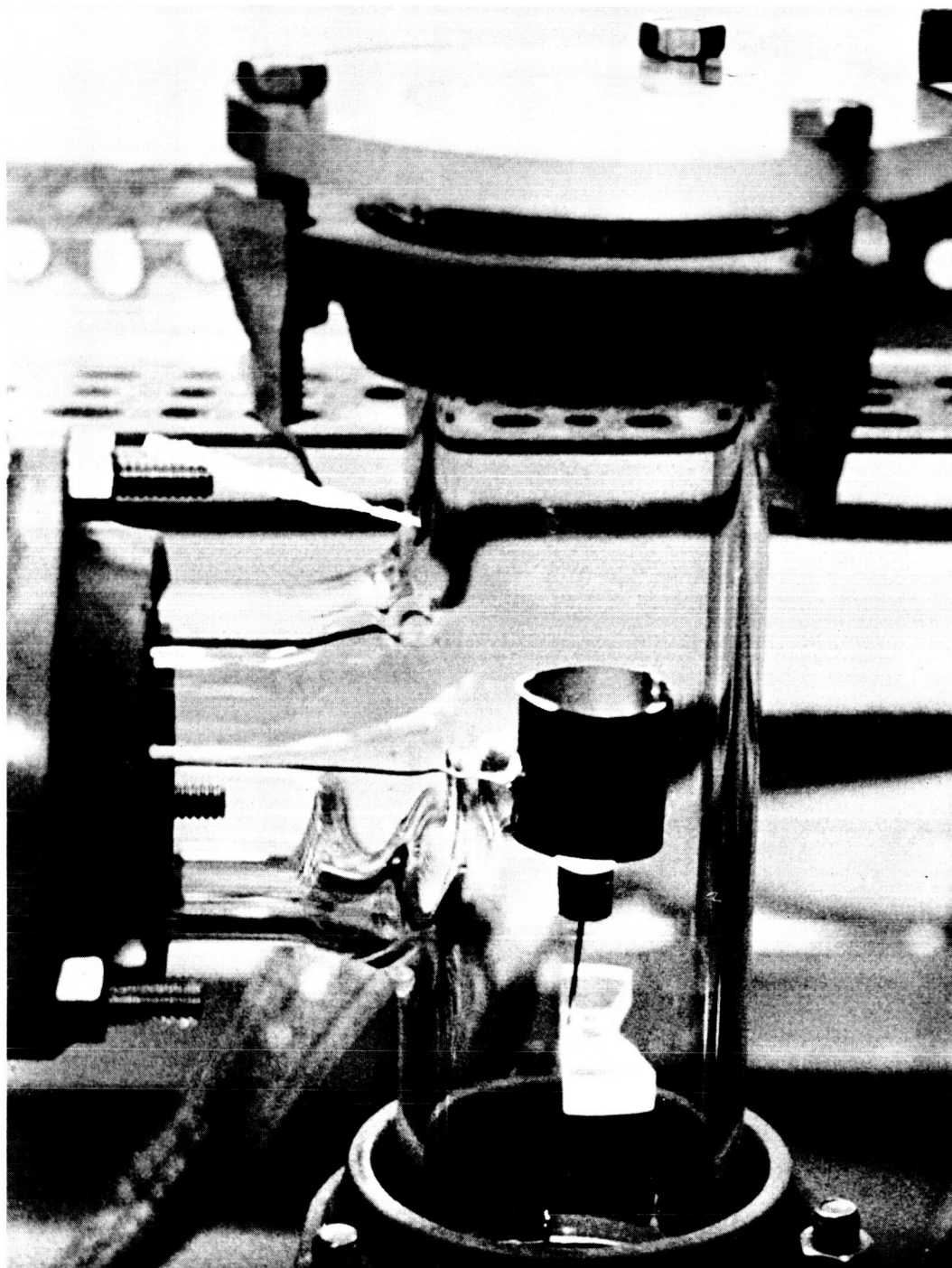


Fig. 2 Specimen in Cathode Sleeve

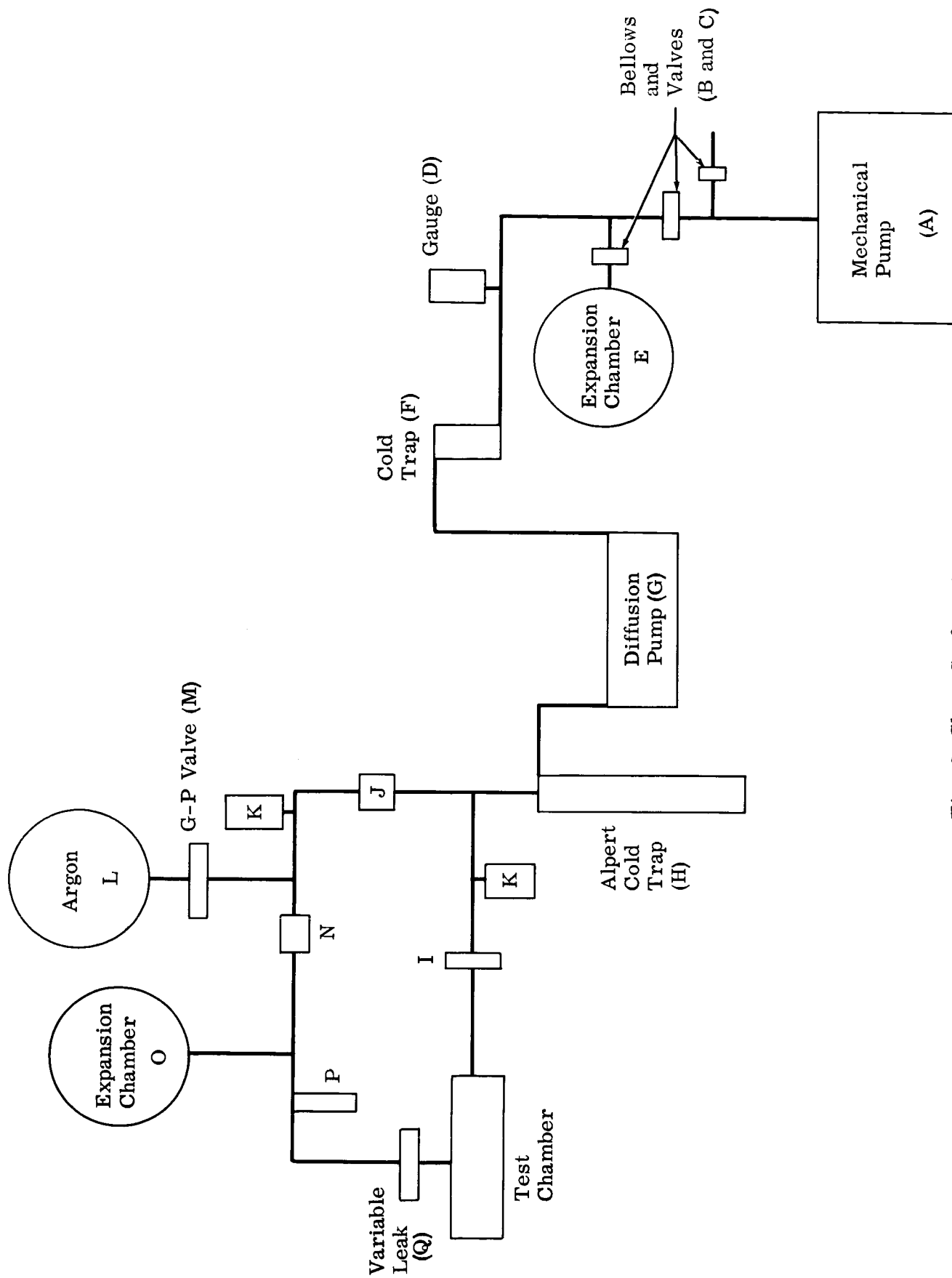


Fig. 3 Clean Surface Apparatus